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(54) Title: A METHOD FOR THE ADHESION OF VINYLIDENE FLUORIDE RESINS TO METAL SUBSTRATES, AND AN ELECTRODE STRUCTURE AND ITS METHOD OF PRODUCTION			
(57) Abstract			
<p>A method for the adhesion of vinylidene fluoride resins to metal substrates which is characterized in that, when sticking polyvinylidene fluoride resin to a metal substrate, (a) vinylidene fluoride resin, (b) at least one type of polymer selected from acrylic and methacrylic polymers with functional groups which exhibit bonding properties or affinity in terms of metals, and (c) an organic compound with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group, are added to and mixed with vinylidene fluoride resin; an electrode constructed using said method for a battery electrode where an electrode constitutional material layer comprising electrode active material and binder is formed on at least one surface of a current collector; and a non-aqueous battery employing said electrode.</p>			

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**A METHOD FOR THE ADHESION OF VINYLIDENE FLUORIDE RESINS TO  
METAL SUBSTRATES, AND AN ELECTRODE STRUCTURE  
AND ITS METHOD OF PRODUCTION**

5           The present invention relates to a method for the  
adhesion/lamination of vinylidene fluoride resins and metals which are  
inherently non-adhesive thereto, and it can be applied to steel pipe linings,  
chemical plant components, and binders for the electrodes of batteries,  
etc, where corrosion resistance, weathering resistance or chemical  
10 resistance is demanded.

[Prior-Art]

          As fluoropolymers of outstanding weatherability and chemical  
15 resistance, etc, which can be melted and moulded, polyvinylidene fluoride  
and vinylidene fluoride copolymer resins are used as coating materials and  
for electrical/electronic components, steel pipe linings, chemical plant  
components and weather-resistant/stain-resistant films, etc. However,  
since they have practically no adhesion properties in terms of other  
20 materials, they suffer from the problem of being difficult to modify or  
composite with other materials.

          Hence, various attempts have been made to confer hydro-philicity,  
and enhance the adhesion, dyeing and dispersion properties and also  
introduce crosslinking sites, etc, by introducing carboxylic acid groups into  
25 the polyvinylidene fluoride resin. For example, as a method of introducing  
carboxylic acid groups, there is known the direct introduction method by  
the copolymerization with the vinylidene fluoride monomer of a monomer  
which has a carboxylic acid group, or a group which can be converted  
thereto, such as acrylic acid, methacrylic acid or the esters thereof (see  
30 Japanese Examined Patent Publication No. 2-604, and elsewhere).

          However, where this approach has been adopted at the time of the  
production of polyvinylidene fluoride resins containing carboxylic acid  
groups, there has been the problem that, on account of the  
copolymerization characteristics with fluorine-containing monomers, etc,  
35 the polymerization rate may be considerably lowered and only low  
molecular weight material obtained unless there is used a special carboxyl-  
group-containing monomer requiring a complex production process.

Moreover, by introducing a copolymer component, the inherent properties of the polymer may no longer be obtained.

In Japanese Unexamined Patent Publication No. 50-41791, there is disclosed a method of grafting a carboxyl-group-containing fluoromonomer while irradiating with ionizing radiation but, in addition to the industrial difficulties of handling radiation, this method also has the problem of decomposition of the polymer main chains or of a crosslinking reaction occurring at the same time. Thus, in the case of the examples attempted hitherto in relation to fluorine-containing polymers, all have had accompanying difficulties when carried out industrially.

Now, turning to the lithium secondary batteries which have come to be employed in portable equipment such as mobile phones, video cameras and notebook-type computers, etc, in recent years, there can be used as the negative electrode active material therein a carbonaceous material such as coke or graphite which undergoes lithium ion doping and un-doping (Japanese Unexamined Patent Publication No. 62-90863), and as the positive electrode active material there can be used transition metal oxides such as manganese oxide and vanadium pentoxide, transition metal sulphides such as iron sulphide and titanium sulphide, and composite compounds of these with lithium (e.g. lithium cobalt composite oxide, lithium cobalt nickel composite oxide and lithium manganese oxide), etc. In such circumstances, the electrodes are obtained by mixing a solvent with the mixture obtained by adding a suitable quantity of a binding agent to the powder-form electrode active material, to produce a paste, which is then coated onto a current collector, and dried, followed by press-bonding.

The binding agent employed in such secondary battery electrodes needs to have resistance to the organic solvent used in the electrolyte and resistance to the active species produced by the electrode reaction. Furthermore, solubility in a specified solvent is required from the point of view of the electrode production process. Polyvinylidene fluoride (PVDF) resin is employed in most cases as a binding agent which satisfies these requirements. However, PVDF resin has inherently poor adhesion to metals and, in the case of both the negative and positive electrodes, the adhesive strength between the current collector and the active material is inadequate following the press-bonding of the active material to the current collector, so there has been the problem that the active material tends to separate away from the current collector and the cycling characteristics of the battery deteriorate.

As a method for improving the bonding between the current collector and electrode active material, there has been proposed roughening the current collector surface (Japanese Unexamined Patent Publication No. 5-6766), but here too the adhesion still cannot be said to be adequate and a further improvement is required. Again, a copolymer of vinylidene fluoride and monomer containing a carboxylic acid group has been proposed (Japanese Unexamined Patent Publication No. 6-172452) but, normally, the copolymerization of a fluoro-monomer and some other monomer which has a carboxylic acid group is not easy, and raising production levels is difficult, so this approach cannot be said to be practical. Moreover, there has been proposed the method of adding to the paste-form electrode mixture a sulphur-containing organic compound which has a mercapto group or the like (Japanese Unexamined Patent Publication Nos 9-82311 and 9-82314), the method of using as a binder a mixture of a functional group-containing acrylic resin or PVDF copolymer, or both, plus PVDF resin (Japanese Unexamined Patent Publication Nos 9-199132, 9-199134 and 9-199130), but even stronger adhesion is demanded than that obtained by these methods.

[Problem to be Resolved by the Invention]

The present invention has the objective of offering a metal-adhesive vinylidene fluoride resin composition where metal adhesion is introduced by a simple method and without impairing the solvent resistance and mechanical and thermal properties inherently possessed by the vinylidene fluoride resin, and also of offering an electrode structure in which the adhesion between the electrode active material and the current collector is enhanced by using this composition as an electrode binding agent for batteries.

[Means for Resolving the Problem]

The present inventors have found that a composition composed of three components, namely a vinylidene fluoride resin, an acrylic and/or methacrylic polymer having functional groups with bonding properties or affinity in respect of metals, and an organic compound with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group, at a specified

compositional ratio, exhibits adhesion properties in respect of metal materials, and they have discovered that not only are such properties valuable in the production of composite materials comprising PVDF resins and metals, but they are also valuable in a binder used for stably fixing an electrode active material to the current collector.

Specifically, the present invention relates to a method for the adhesion of vinylidene fluoride resins to metal substrates which is characterized in that, when sticking a vinylidene fluoride resin to a metal substrate, vinylidene fluoride resin (a), at least one type of polymer (b) selected from acrylic and methacrylic polymers with functional groups which exhibit bonding properties or affinity in terms of metals, or an acrylic or methacrylic resin composition containing such polymer, and an organic compound (c) with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group, are added to and mixed with vinylidene fluoride resin (a).

The vinylidene fluoride resin referred to here can be selected from vinylidene fluoride homopolymer and copolymers (vinylidene fluoride copolymers) of vinylidene fluoride with other monomers which can copolymerize with vinylidene fluoride, and these resins can be used on their own or as mixtures of two or more types.

The vinylidene fluoride copolymers should have from 50 to 98 wt% vinylidene fluoride component in the copolymer, and more desirably from 75 to 96 wt%. Fluoromonomers such as tetrafluoroethylene, hexafluoropropylene, tri-fluoroethylene and trifluorochloroethylene, etc, are preferred as the other monomer copolymerizable with the vinylidene fluoride, and one or more than one of these can be used. In particular, in the case where there is employed a mixture of vinylidene fluoride homopolymer and vinylidene fluoride copolymer, it is preferred that the vinylidene fluoride copolymer has a vinylidene fluoride component content of 75 to 96 wt%, and has a flexural modulus at room temperature (23°C) of no more than 1000 MPa and a breaking elongation of at least 50 wt%.

These vinylidene fluoride resins are obtained by the polymerization of the vinylidene fluoride monomer and other monomer by a known suspension polymerization method or emulsion polymerization method, etc (literature example: "Fluororesin Handbook", Edited by Satogawa, Published by Nikkan Kogyo Shinbunsha 1990). Methods for the copolymerization of vinylidene fluoride monomer and other monomer are described in, for example, US Patent Nos 4,076,929 and 4,569,978, and

in Japanese Unexamined Patent Publication No. 6-336510). In such circumstances, it is possible to vary the monomer compositional distribution of the copolymer obtained by control of the monomer, chain transfer agent and polymerization initiator addition methods. In Japanese  
5 Unexamined Patent Publication No. 6-336510, there is described a method for obtaining a mixture of vinylidene fluoride homopolymer and copolymer at the polymerization stage, and polymer obtained thereby is favourably employed as the vinylidene fluoride resin of the present invention. It is preferred that all such vinylidene fluoride polymers employed in the present  
10 invention have a melt flow rate (MFR) under a 2.16 kg load at 230°C of from 0.003 to 300 g/10 minutes, and more preferably from 0.01 to 30 g/10 minutes.

In the present invention, as the (a) component, it is also possible to use a mixture of from 1 to 99 wt% vinylidene fluoride homopolymer and  
15 from 99 to 1 wt% vinylidene fluoride copolymer resin. Properties such as the resin flexibility and the solvent resistance can be varied according to the mixing ratio thereof (that is to say, by increasing the proportion of the vinylidene fluoride copolymer, the flexibility is increased, while, on the other hand, swelling by solvents is also increased) and there can be  
20 employed an optimal combination in accordance with the objectives.

The acrylic or methacrylic polymer with functional groups which exhibit bonding properties or affinity in terms of metals, which is used as component (b) in the present invention, is a polymer in which the chief component is an alkyl acrylate or alkyl methacrylate and which has at least  
25 in one position in the main chain, side chains or at chain ends, a functional group which exhibits bonding properties or affinity in terms of metals. As examples of such polymers, there are the random copolymers, block copolymers and graft polymers produced by methods such as radical polymerization, ionic polymerization or co-ordination polymerization, from  
30 at least one type of monomer selected from alkyl acrylates and alkyl methacrylates, plus monomer with a functional group which exhibits bonding properties or affinity in respect of metals.

As examples of the functional groups possessed by the (b) component, which exhibit bonding properties or affinity in respect of  
35 metals, there can be cited carboxylic acid groups or carboxylic acid anhydride groups, epoxy groups (glycidyl groups), mercapto groups, sulphide groups, oxazoline groups, phenolic groups and ester groups, etc.

One example of an aforesaid acrylic or methacrylic polymer is the copolymer of at least one type of monomer selected from those with a carboxylic acid group or carboxylic acid anhydride group, and an alkyl acrylate and/or alkyl methacrylate. In such circumstances, specific  
5 examples of the alkyl acrylate and alkyl methacrylate are methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate, etc. Further, as specific examples of the monomer with a carboxylic acid group or carboxylic acid anhydride group, there are acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid,  
10 alkenylsuccinic acid, acrylamido-glycolic acid, allyl 1,2-cyclohexanedicarboxylate and other such unsaturated carboxylic acids, and maleic anhydride, alkenylsuccinic anhydride and other such unsaturated carboxylic acid anhydrides, etc.

Further, it is preferred that at least 50 wt%, and more desirably  
15 from 70 wt% to 99 wt%, of this acrylic or methacrylic polymer be composed of at least one type of monomer selected from alkyl acrylates and alkyl methacrylates. The amount of the contained functional groups which exhibit bonding properties or affinity in respect of metals will preferably be from 0.01 to 2 moles per 1 kg of the acrylic or methacrylic  
20 polymer. In the case where this polymer component is a copolymer of at least one monomer selected from alkyl acrylates and alkyl methacrylates and monomer having a carboxylic acid group or carboxylic acid anhydride group, the proportion of the monomer with a carboxylic acid group or carboxylic acid anhydride group will preferably be from 0.2 to 30 wt% of  
25 said copolymer, and more preferably from 1 to 20 wt%. Furthermore, as a constituent component, there may also be included in the molecular chain, besides the above, vinyl monomer such as styrene, or modified units such as imides, but the amount of these will be no more than 50 wt%, and preferably no more than 30 wt% of said polymer.

30 Component (b) used in the present invention may also be a composition composed of an acrylic or methacrylic polymer which does not possess special functional groups and an aforesaid acrylic or methacrylic polymer having functional groups which show bonding properties or affinity in terms of metals.

35 Whereas the (b) component is a polymer, the organic compound with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group used as component (c) in the present invention is a comparatively low

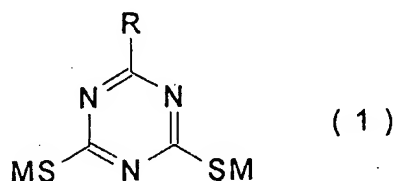


molecular weight compound. Its molecular weight range is up to 5000, preferably up to 2000 and more preferably from 60 to 1000.

Of these, as a sulphur-containing compound with a mercapto group, there is preferred an organic compound with a plurality (2 to 6) of mercapto groups in the molecule, or a mercapto carboxylic acid with at least one mercapto group and at least one carboxylic acid group, or a mercapto carboxylic acid ester with at least one mercapto group and at least one ester group, or a mercapto sulphide group with at least one mercapto group and at least one thiol group.

From amongst these, as examples of organic compounds with a plurality of mercapto groups in the molecule, there are ethanedithiol, 1,3-propanedithiol, hexanedithiol, penta-erythrithiol, dimercaptodiethyl ether, 1,8-dimercapto-3,6-dioxaoctane, and 1,5- or 2,7-dimercaptonaphthalene, etc. Further, as examples of mercapto-carboxylic acids, there are thioglycolic acid and 3-mercaptopropionic acid. As examples of mercapto-carboxylic acid esters, there are 2-ethylhexyl  $\beta$ -mercaptopropionate, 3-methoxybutyl  $\beta$ -mercaptopropionate, trimethylolpropane-tris( $\beta$ -thiopropionate), pentaerythritetra(mercaptopropionate ester) and other such mercaptopropionic acid derivatives, 2-ethylhexyl thioglycolate, isooctyl thioglycolate, butyl thioglycolate, methoxybutyl thioglycolate, trimethylolpropanetris(thioglycolate) and other such thioglycolic acid derivatives. As examples of mercapto sulphides, there are 2,2'-dimercaptodiethylsulphide and bis-(2-mercaptoethyl)sulphide.

Furthermore, as the (c) component, there can also be favourably used the 2-substituted-4,6-dimercapto-1,3,5-triazine derivatives represented by following Structural Formula 1 :



[Here, R denotes  $\text{OR}_1$ ,  $\text{SR}_2$  or  $\text{NR}_1\text{R}_2$  (where  $\text{R}_1$  and  $\text{R}_2$  are the same or different and represent hydrogen, an alkyl group, cycloalkyl group, alkenyl group, aryl group, arylalkyl group or alkylaryl group), and M denotes hydrogen, an alkali metal or alkaline earth metal.]

As examples of the alkyl group here, there are the methyl, ethyl, propyl, butyl, t-butyl, pentyl, hexyl, octyl, nonyl, 2-ethylhexyl, dodecyl and octadecyl groups; as examples of the alkenyl group, there are the allyl and oleyl groups; as examples of the arylalkyl group, there are the benzyl, methylbenzyl, phenylethyl and phenyl-propyl groups; as examples of the aryl group, there are the phenyl and naphthyl groups; and as examples of the alkylaryl group, there are the ethylphenyl, butylphenyl octylphenyl and 4'-hydroxy-3',5'-di-t-butylphenyl groups.

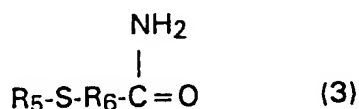
The organic compound with a thioether group employed as the (c) component in the present invention desirably has at least one functional group selected from the carboxylic acid group, carboxylic acid anhydride group, ester group and amide group, as well as this thioether group. Of these, as examples of thioethers with a carboxylic acid group or carboxylic acid anhydride group, there are 3,3'-thiodipropionic acid, carboxyethylthiosuccinic acid, carboxyethylthiosuccinic anhydride and hydroxyethylthiopropionic acid. Further, as examples of thioethers with an ester group, there are dilauryl thiodipropionate, distearyl thiodipropionate, dioctadecyl thiodipropionate, ditetradecyl thiodipropionate and di-dodecyl thiodipropionate. As an example of a thioether with an amide group, there is hydroxyethylthio-propionamide.

In the present invention, there is especially desirably used as the organic compound with a thioether group, a thioethercarboxylic acid represented by the following formula 2, or anhydride thereof,



(where  $\text{R}_3$  and  $\text{R}_4$  are  $\text{C}_2$  to  $\text{C}_{20}$  hydrocarbon groups, and  $m$  and  $n$  are the same or different integer in the range 1 to 4), and still more preferably it is carboxyethyl-thiosuccinic acid or carboxyethylthiosuccinic anhydride.

As thioethers with an amide group, there are the thioetheramides represented by the following formula 3 :



(where  $R_5$  and  $R_6$  are  $C_2$  to  $C_{20}$  hydrocarbon groups), an example of which is hydroxyethylthiopropionamide.

Furthermore, as component (c), it is possible to use an organic compound with at least one functional group selected from carboxylic acid and carboxylic acid anhydride groups. As examples thereof, there are  
5 acetic acid, acrylic acid, formic acid, citric acid, oxalic acid, lactic acid, maleic acid, propionic acid, malonic acid and butyric acid, etc.

The vinylidene fluoride resin composition with improved metal adhesion of the present invention contains, per 100 parts by weight of (a)  
10 vinylidene fluoride resin, from 0.5 to 50 parts by weight and more preferably from 1 to 20 parts by weight of (b) acrylic or methacrylic polymer with functional groups which exhibit bonding properties or affinity in terms of metals, and from 0.01 to 5 parts by weight and more preferably 0.03 to 1 part by weight of (c) an organic compound with at  
15 least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group. In cases where the added amount of the (b) component or the (c) component is too low, there is an insufficient effect in improving the adhesion between metal and vinylidene fluoride resin composition, while, if there is  
20 too much, then the mechanical properties, chemical resistance and solvent resistance, etc, inherently possessed by the vinylidene fluoride resin are impaired.

In the present invention, in particular in the case where the adhesion process is a solution application method, it is preferred that the  
25 vinylidene fluoride resin contain from 1 to 15 wt% vinylidene fluoride copolymer, and per 100 parts by weight of the vinylidene fluoride resin there is desirably added from 0.5 to 10 parts by weight and more preferably 1 to 5 parts by weight of the (b) component acrylic or methacrylic polymer, and from 0.03 to 1 part by weight of the (c)  
30 component organic compound.

Furthermore, the vinylidene fluoride resin composition with metal adhesion improved by the above method can be used as an adhesive agent when sticking a vinylidene fluoride resin to a metal. In such  
circumstances, the vinylidene fluoride resin used in the adhesive agent  
35 need not necessarily be composed of the same resin as the vinylidene fluoride resin which forms the surface layer.

The metal-adhesive composition of the present invention is produced by a solution process or melt process. In the case of a solution

process, the aforesaid three components (a), (b) and (c) may be dissolved in the prescribed proportions in a solvent such as N-methylpyrrolidone, N,N-dimethylformamide, tetrahydro-furan, dimethylacetamide, dimethylsulphoxide, hexamethyl-phosphoramide, tetramethylurea, acetone, methyl ethyl ketone or the like, at a temperature lower than the boiling point of the solvent used. In the case of a melt process, production can be carried out by a conventional method of heating and mixing the three components (a), (b) and (c) in the prescribed proportions using a screw mixing machine. Here, conventionally-known methods can be used for the method of melting and mixing, such as a Banbury mixer, rubber mill or single or twin-screw extruder, etc, and normally the resin composition is obtained by melting and mixing at 100 to 300°C and preferably, although it will also depend on the composition, 150 to 260°C.

Examples of the metal materials employed as the adhesion substrate in the present invention are iron, stainless steel, aluminium, copper, nickel, titanium, lead, silver, chromium, and alloys of various kinds, etc, and the form thereof is not particularly restricted.

#### [Action]

As explained above, by means of the present invention it becomes possible to improve easily the adhesion of vinylidene fluoride resins and metal materials, and to obtain easily composite materials of a metal material and a vinylidene fluoride resin. The composite materials obtained by this method can have various forms such as film, sheet, plate, pipe, rod, strand, monofilament or fibre, and the means of production thereof include calendering, extrusion lamination, multilayer injection, fluid immersion coating, dipping, spray coating and melt-pressing, etc. The method of the present invention can also be employed for fluoro-coating materials using vinylidene fluoride resin dissolved or dispersed in a solvent, and for electric wire coating by means of vinylidene fluoride resin.

Moreover, the method of the present invention for the adhesion of polyvinylidene fluoride resin to a metal substrate can also be applied to the production of a battery electrode structure where an electrode constitutional material layer comprising at least electrode active material and binder is formed on the surface of a current collector and, in this way, the adhesion between the electrode active material and the current collector is improved, so that not only is it possible to prevent the

dropping away of electrode active material from the current collector during battery production, but it is also possible to obtain an electrode for a battery of finally improved cycle characteristics. In particular, this is useful in an electrode binder for non-aqueous type secondary batteries  
5 such as lithium ion secondary batteries.

In such circumstances, as the electrode current collector, there may be used a metal foil, metal mesh or three-dimensional porous body, etc, but it is preferred that the metal employed in the current collector be a metal which cannot readily alloy with lithium, in particular, iron, nickel,  
10 cobalt, copper, aluminium, titanium, vanadium, chromium and manganese, employed on their own or as alloys thereof.

Of the electrode active materials, the negative electrode active material should be a material which can undergo doping and undoping by lithium ions. Examples of such materials are coke materials like petroleum-based or carbon-based coke, acetylene black or other such carbon black,  
15 graphite, glassy carbon, active carbon, carbon fibre and carbonaceous materials such as fired organic polymers obtained by the firing of organic high polymers in a non-oxidizing atmosphere. Moreover, copper oxide may also sometimes be added thereto.

20 As positive electrode active materials, there are the aforementioned generally-used materials and there are no particular restrictions. An electro-conductor may also be added thereto.

As an example of the electrode production process, a slurry obtained by mixing, in the presence of solvent, a specified amount of the electrode active material and, as the binding agent, (a) aforesaid vinylidene  
25 fluoride resin, (b) aforesaid acrylic or methacrylic polymer with functional groups showing bonding properties or affinity in terms of metals, and (c) aforesaid organic compound with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group, is coated onto the current collector, after  
30 which drying is performed, followed by optional pressing, and the electrode obtained. In such circumstances, following the application of the slurry, a heat treatment is desirably carried out at from 60 to 250°C, more preferably from 80 to 200°C, for from 1 minute to 10 hours,  
35 according to the particular requirements. If necessary, electrical conductivity conferring agents and other additives (copper oxide, etc) may also be added to the electrode constitutional material layer.

As the solvent used for obtaining the slurry applied to the electrode current collector, there may be employed organic solvents such as N-methylpyrrolidone, N,N-dimethylformamide, tetrahydrofuran, dimethylacetamide, dimethyl sulphoxide, hexamethylphosphoramide, tetramethylurea, acetone and methyl ethyl ketone, or water, either on their own or as mixtures thereof. Of these, N-methylpyrrolidone is especially desirably used. Further-more, where required, a dispersing agent may be added. In such circumstances, a nonionic dispersing agent is preferably used.

10 The amount of binder (total of (a) and (b) components) added to the electrode active material is preferably from 1 to 50 parts by weight and more preferably from 3 to 40 parts by weight per 100 parts by weight of the electrode active material. The optimum amount thereof added will vary with the battery and the electrode form. The respective proportions  
15 of the (a), (b) and (c) components are as stated above.

The preferred (a) component vinylidene fluoride resin will vary with the properties demanded of the battery or electrode, and selection is made from vinylidene fluoride homopolymer, the aforesaid vinylidene fluoride copolymers, and mixtures of from 1 to 99 wt% vinylidene fluoride  
20 homopolymer and from 99 to 1 wt% vinylidene fluoride co-polymer. For example, in the case of a thin battery or square-shaped battery where flexibility is required of the electrodes, a vinylidene fluoride copolymer such as a copolymer of vinylidene fluoride and hexafluoropropylene, or a mixture of such vinylidene fluoride copolymer and vinylidene fluoride  
25 homopolymer is desirably used. In the case where flexibility is regarded as not all that necessary, vinylidene fluoride homopolymer is desirably used. In each case where a vinylidene fluoride resin is used, the method of the present invention is effective in enhancing the adhesion between current collector and electrode active material. In particular, in the case where the  
30 (a) component is a mixture of 80 to 99 wt% vinylidene fluoride homopolymer and 20 to 1 wt% vinylidene fluoride copolymer resin, the swelling in terms of the carbonate solvents normally used in a lithium battery is about the same as that for vinylidene fluoride homopolymer, but the flexibility is improved when compared to vinylidene fluoride  
35 homopolymer, so such a mixture is preferably employed in a liquid type lithium battery.

The negative electrode structure and positive electrode structure produced as described above are arranged with a liquid-permeable

separator (for example polyethylene or polypropylene porous film) disposed between them, and then by impregnating this with a non-aqueous type electrolyte, there is formed a non-aqueous type secondary battery. Furthermore, a cylindrical secondary battery can be obtained by winding, in the form of a roll (a helical shape), a laminate comprising the negative electrode structure with an active layer formed on both faces/separator/positive electrode structure with an active layer formed on both faces/separator, then introducing the structure thus obtained into a metal casing with a bottom, connecting the negative electrode to the negative electrode terminal and the positive electrode to the positive electrode terminal, and impregnating with electrolyte, after which the casing is sealed.

In regard to the electrolyte liquid employed here, in the case of a lithium ion secondary battery for example, there is employed a lithium salt as the electrolyte dissolved in a non-aqueous organic solvent at a concentration of about 1 M. As examples of the lithium salt, there are  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiSO}_3\text{CF}_3$  and  $\text{Li}[(\text{SO}_2\text{CF}_3)_2\text{N}]$ , etc. Furthermore, as the non-aqueous organic solvent, there can be employed propylene carbonate, ethylene carbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, dimethyl carbonate, diethyl carbonate and methyl ethyl carbonate, etc, either on their own or as mixtures of two or more.

Below, the present invention is explained by means of examples, but the invention is not to be restricted in any way by the said examples.

## Examples

### Example 1

A solution (S-1) formed by dissolving 97 g of Kynar 461, which is a vinylidene fluoride homopolymer produced by Elf Atochem (MFR at  $230^\circ\text{C}$  under a 2.16kg load = 0.03 g/10 min, flexural modulus at  $23^\circ\text{C}$  = 1500 MPa), 3 g of polymethyl methacrylate in which carboxylic acid anhydride groups had been introduced (Sumipex TR, made by Sumitomo Chemical Co.) and 0.3 g of 2,4,6-trimercapto-1,3,5-triazine, in 900 g of N-methylpyrrolidone (NMP), was applied onto 1 mm thickness aluminium sheet and copper sheet and, after leaving for 1 hour at  $120^\circ\text{C}$ , drying was carried out under reduced pressure.

When a cross-cut adhesion test (based on JIS K5400 6.15) was carried out after cutting the polymer coating surface obtained at spacings of 1 mm, the residual adhering percentage of polymer coated layer was 100% for both the aluminium and the copper sheets. Furthermore, when  
5 a tape peeling test was conducted, the residual adhering percentage was 85% on the aluminium sheet and 100% on the copper sheet. It was confirmed that there was good adhesion between the aforesaid vinylidene fluoride resin composition and the metal sheets. Further, after immersion  
10 for 72 hours at 60°C in ethylene carbonate, the degree of swelling of the polymer layer by the solvent was 24%, which was about the same as the value for vinylidene fluoride homopolymer.

#### Example 2

15 Excepting that, as the vinylidene fluoride resin in Example 1, there was used Kynar 2801 which is copolymer of vinylidene fluoride and hexafluoropropylene made by Elf Atochem (hexafluoropropylene content = 10 wt%, MFR at 230°C under a 2.16 kg load = 0.2 g/10 min, flexural modulus at 23°C = 600 MPa), instead of the Kynar 461, an NMP solution  
20 (S-2) was produced in the same way as in Example 1. As a result of the same cross-cut adhesion test, the residual adhering percentage was 100% for both the aluminium and copper sheets. Furthermore, in the tape peeling test, the residual adhering percentage was 90% on the aluminium sheet and 100% on the copper sheet.

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#### Example 3

A solution (S-3) formed by dissolving 87 g of Kynar 301F which is a vinylidene fluoride homopolymer produced by Elf Atochem (MFR at  
30 230°C under a 2.16 kg load = 0.03 g/10 min), 10 g of the copolymer of vinylidene fluoride and hexafluoropropylene, Kynar 2801, described in Example 2, 3 g of Sumipex TR described in Example 1 and 0.1 g of 2,4,6-trimercapto-1,3,5-triazine in 900g of NMP, was applied onto 1 mm thickness aluminium sheet and copper sheet and left for 1 hour at 120°C,  
35 after which drying was carried out under reduced pressure.

When a cross-cut adhesion test (based on JIS K5400 6.15) was carried out after cutting the polymer coating obtained at spacings of 1 mm, the residual adhering percentage of polymer coated layer was



100% for both the aluminium and the copper sheets. Furthermore, when a tape peeling test was conducted, the residual adhering percentage was 100% for both the aluminium and copper sheets. It was confirmed that there was good adhesion between the aforesaid vinylidene fluoride resin  
5 composition and the metal sheets. Furthermore, after immersion for 72 hours at 60°C in ethylene carbonate, the degree of swelling of the polymer layer by the solvent was 26%, and while this was slightly greater than that of pure Kynar 301F, no great change was apparent.

#### 10 Example 4

A solution (S-4) was prepared by dissolving 48 g of Kynar 301F, 48 g of the copolymer of vinylidene fluoride and hexafluoropropylene, Kynar 2801, described in Example 2, 4 g of the Sumipex TR described in  
15 Example 1 and 0.6 g of 2,4,6-trimercapto-1,3,5-triazine in 900g of NMP. As a result of a cross-cut adhesion test carried out in the same way as in Example 3, the residual adhering percentage was 100% for both the aluminium and copper sheets. Furthermore, in the tape peeling test, the residual adhering percentage was 100% for both the aluminium and  
20 copper sheets.

#### Example 5

An NMP solution (S-5) was prepared in the same way as in  
25 Example 3, excepting that the 2,4,6-trimercapto-1,3,5-triazine was replaced by 3-mercaptopropionic acid. As a result of an identical cross-cut adhesion test, the residual adhering percentage was 100% for both the aluminium and copper sheets. Furthermore, in the tape peeling test, the residual adhering percentage was 95% for the aluminium sheet and 100%  
30 for the copper sheet.

#### Example 6

An NMP solution (S-6) was prepared in the same way as in  
35 Example 3, excepting that the 2,4,6-trimercapto-1,3,5-triazine was replaced by carboxyethylthiosuccinic anhydride. As a result of an identical cross-cut adhesion test, the residual adhering percentage of polymer coating layer was 100% for both the aluminium and copper sheets.

Furthermore, in the tape peeling test, the residual adhering percentage was 100% for both the aluminium and copper sheets.

#### Example 7

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An NMP solution (S-7) was prepared in the same way as in Example 3 excepting that, as the acrylic polymer with functional groups having bonding properties or affinity in terms of metals, there was used a copolymer comprising maleic anhydride, N-methyldimethylglutarimide, 10 monomer containing carboxylic acid, and methyl methacrylate (Paraloid EXL4151, produced by Rohm and Haas). As a result of an identical cross-cut adhesion test, the residual adhering percentage of polymer coating layer was 100% for both the aluminium and copper sheets, and in the tape peeling test too, the residual adhering percentage was 100% for both 15 the aluminium and copper sheets.

#### Example 8

An NMP solution (S-8) was prepared in the same way as in 20 Example 3 excepting that, as an acrylic polymer with functional groups having bonding properties or affinity in terms of metals, there was employed an epoxy-modified polymethyl methacrylate grafted polymethyl methacrylate (*Rezeda* GP-301, Toagosei Chemical Industry Co.). As a result of an identical cross-cut adhesion test, the residual adhering 25 percentage of polymer coating layer was 100% for both the aluminium and copper sheets and, in the tape peeling test too, the residual adhering percentage was 100% for both the aluminium and copper sheets.

#### [Example 9]

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As a negative electrode active material support, 100 g of coal pitch coke which had been pulverized in a ball mill was dispersed in 100 g of NMP solution (S-1) obtained in Example 1, to produce a slurry (paste). This slurry was coated onto one face of copper foil of thickness 20  $\mu\text{m}$  as 35 the current collector, then dried for 15 minutes at 130°C, to produce an electrode structure of thickness 110  $\mu\text{m}$  and width 20 mm (to be used as a negative electrode).

Adhesive tape was affixed to the electrode active layer on this electrode surface, and when the adhesive strength between current collector and electrode active layer was measured, by means of a tensile tester, it was 185 g/cm. Further, after peeling, considerable remaining  
5 adhered electrode active material was noted on the current collector, confirming that the adhesion between electrode active material and current collector was extremely good. Moreover, in an adhesion test carried out by winding in the form of a roll on a 1 mm diameter cylinder, absolutely no separation of the electrode active layer was noted and, subsequently, after  
10 immersing the electrode in ethylene carbonate and leaving for 3 days at 60°C, absolutely no separation of electrode active layer was noted.

#### Example 10

15 An electrode structure was prepared in the same way as in Example 9, except that there was used S-2 obtained in Example 2 as the NMP solution in Example 9. The adhesive strength between the current collector and the electrode active layer was 190 g/cm, and in the other tests too good adhesion was confirmed.

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#### Example 11

An electrode structure was prepared in the same way as in Example 9, except that there was used S-3 obtained in Example 3 as the  
25 NMP solution in Example 9. The adhesive strength between the current collector and the electrode active layer was 300 g/cm, and in the other tests too good adhesion was confirmed.

#### Example 12

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94 g of  $\text{LiCoO}_2$  as the positive electrode active material, 6 g of graphite as an electrical conductor and, as a binder, 100 g of the NMP solution (S-3) obtained in Example 3, were mixed together to produce a slurry (paste). This slurry was applied to one face of a 20  $\mu\text{m}$  thickness  
35 aluminium foil as the current collector, and dried for 15 minutes at 130°C, to produce an electrode structure (to be used as a positive electrode) of thickness 100  $\mu\text{m}$  and width 20 mm. The adhesive strength between the current collector and the electrode active material was 230 g/cm and in the other tests too good adhesion was confirmed.

### Comparative Example 1

A solution (S-9) formed by dissolving 100 g of polyvinylidene fluoride (Kynar 301F) in 900 g of NMP was applied onto 1 mm thickness aluminium sheet and copper sheet, then left for 1 hour at 120°C and further dried under reduced pressure. When a cross-cut adhesion test was carried out in the same way as in Example 1 as an adhesion test on this polymer coated layer, the residual percentage of adhering polymer coated layer was less than 20% for both the aluminium and copper sheets. Furthermore, when a tape peeling test was carried out, the polymer layer completely separated away. Moreover, when the degree of swelling by ethylene carbonate was measured by the same method as in Example 1 using polymer which had separated away from the metal sheets, it was 23%.

### Comparative Example 2

A solution (S-10) formed by dissolving 97 g of polyvinylidene fluoride (Kynar 461) and 3 g of the Sumipex TR described in Example 1 in 900 g of NMP was applied onto 1 mm thickness aluminium sheet and copper sheet, then left for 1 hour at 120°C and further dried under reduced pressure. When a cross-cut adhesion test was carried out in the same way as in Example 1 as an adhesion test on this polymer coated layer, the residual percentage of adhering polymer coated layer was 100% for both the aluminium and copper sheets but, in the tape peeling test, the residual adhering percentage was about 50% on the aluminium sheet and about 80% on the copper sheet. Further, the degree of swelling by ethylene carbonate of the polymer layer, measured by the same method as in Example 1, was 24%.

### Comparative Example 3

A solution (S-11) formed by dissolving 100 g of Kynar 461 and 0.3 g of 2,4,6-trimercapto-1,3,5-triazine in 900 g of NMP was applied onto 1 mm thickness aluminium sheet and copper sheet, then left for 1 hour at 120°C, and further dried under reduced pressure. When a cross-cut adhesion test was carried out in the same way as in Example 1 as an adhesion test on this polymer coated layer, the residual percentage of

adhering polymer coated layer was about 70% on the aluminium sheet and about 90% on the copper sheet but, in the tape peeling test, the residual adhering percentage was about 30% on the aluminium sheet and about 50% on the copper sheet. The degree of swelling by ethylene carbonate of the polymer layer, measured by the same method as in Example 1, was 23%.

#### Comparative Example 4

10 A solution (S-12) formed by dissolving 97 g of copolymer of vinylidene fluoride and hexafluoropropylene (Kynar 2801) and 3 g of Sumipex TR in 900 g of NMP was applied onto 1 mm thickness aluminium sheet and copper sheet, then left for 1 hour at 120°C, and further dried under reduced pressure. When a cross-cut adhesion test was carried out  
15 in the same way as in Example 1 as an adhesion test on this polymer coated layer, the residual percentage of adhering polymer coated layer was 100% for both the aluminium and copper sheets whereas, in the tape peeling test, the residual adhering percentage was about 70% on the aluminium sheet and about 90% on the copper sheet. Moreover, the  
20 degree of swelling by ethylene carbonate of the polymer layer, measured by the same method as in Example 1, was 42%.

#### Comparative Example 5

25 A solution (S-13) formed by dissolving 87 g of Kynar 301F, 10 g of Kynar 2801 and 3 g of Sumipex TR in 900 g of NMP was applied onto 1 mm thickness aluminium sheet and copper sheet, then left for 1 hour at 120°C, and further dried under reduced pressure. When a cross-cut adhesion test was carried out in the same way as in Example 1 as an  
30 adhesion test on this polymer coated layer, the residual percentage of adhering polymer coated layer was 100% for both the aluminium and copper sheet whereas, in the tape peeling test, the residual adhering percentage was about 80% on the aluminium sheet and about 100% on the copper sheet. Again, the degree of swelling by ethylene carbonate of  
35 the polymer layer, measured by the same method as in Example 1, was 26%.

### Comparative Example 6

An electrode structure was produced in the same way as in Example 9, excepting that S-9 obtained in Comparative Example 1 was  
5 used as the NMP solution in Example 9. The adhesive strength between the current collector and the electrode active layer was a low value of 35 g/cm. Further, in the roll winding test based on a cylinder of diameter 1 mm, separation of the electrode active layer was noted, and in the immersion test in ethylene carbonate at 60°C, considerable separation of  
10 the electrode active layer occurred.

### Comparative Example 7

An electrode structure was produced in the same way as in  
15 Example 9, excepting that S-10 obtained in Comparative Example 2 was used as the NMP solution in Example 9. The value of the adhesive strength between the current collector and the electrode active layer was not very high, at 70 g/cm. Moreover, in the roll winding test based on a cylinder of diameter 1 mm, separation of the electrode active layer was  
20 noted, and in the immersion test in ethylene carbonate at 60°C, considerable separation of the electrode active layer occurred.

### Comparative Example 8

25 An electrode structure was produced in the same way as in Example 9, excepting that S-11 obtained in Comparative Example 3 was used as the NMP solution in Example 9. The value of the adhesive strength between the current collector and the electrode active layer was not all that high, at 76 g/cm. Moreover, in the roll winding test based on  
30 a cylinder of diameter 1 mm, separation of electrode active layer was noted, albeit slight, and in the immersion test in ethylene carbonate at 60°C, some separation of the electrode active layer occurred.

### Comparative Example 9

35 An electrode structure was produced in the same way as in Example 9, excepting that S-12 obtained in Comparative Example 4 was used as the NMP solution in Example 9. The value of the adhesive strength between the current collector and the electrode active layer was

not all that high, at 80 g/cm. Moreover, in the roll winding test based on a cylinder of diameter 1 mm, some separation of electrode active layer was noted, albeit slight, and in the immersion test in ethylene carbonate at 60°C, some separation of the electrode active layer occurred.

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#### Comparative Example 10

An electrode structure was produced in the same way as in Example 9, excepting that S-13 obtained in Comparative Example 5 was used as the NMP solution in Example 9. The value of the adhesive strength between the current collector and the electrode active layer was rather high, at 210 g/cm but did not reach the value achieved in Example 11 employing solution S-3. Furthermore, while in the roll winding test based on a cylinder of diameter 1 mm and in the immersion test in ethylene carbonate at 60°C, practically no separation of the electrode active layer was noted, the stability was inadequate in the electrode structure production when compared to Example 11.

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#### Effects of the Invention

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By means of the present invention it becomes possible to obtain a metal-adhesive vinylidene fluoride resin composition by a simple method and without impairing the solvent resistance or the mechanical or thermal properties inherently possessed by a vinylidene fluoride resin. When the metal-adhesive vinylidene fluoride resin composition of the present invention is used as a binder for battery electrodes, it becomes possible to produce an electrode structure with high adhesive strength between the electrode active material and current collector. In this way, not only is it possible to prevent separation of the electrode active material and the current collector at the time of battery production, but a secondary battery is obtained which does not show a deterioration in the discharge capacity due to repeated charging and discharging. The method of the present invention is particularly valuable for non-aqueous secondary batteries such as lithium ion secondary batteries, etc.

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### CLAIMS

1. A method for the adhesion of vinylidene fluoride resins to metal substrates which is characterized in that, when sticking a vinylidene fluoride resin to a metal substrate, there are added to and mixed with vinylidene fluoride resin (a) from 0.5 to 50 parts by weight of at least one type of polymer (b) selected from acrylic and methacrylic polymers with functional groups which exhibit bonding properties or affinity in terms of metals, or an acrylic or methacrylic resin composition containing such polymer, and from 0.01 to 5 parts by weight of an organic compound (c) with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group, per 100 parts by weight of vinylidene fluoride resin (a).
2. A method for the adhesion of vinylidene fluoride resins to metal substrates according to Claim 1, where the vinylidene fluoride resin is vinylidene fluoride homopolymer.
3. A method for the adhesion of vinylidene fluoride resins to metal substrates according to Claim 1, where the vinylidene fluoride resin is a copolymer of vinylidene fluoride and at least one monomer selected from tetrafluoroethylene, hexafluoropropylene, trifluoro-ethylene and trifluorochloroethylene, and the percentage vinylidene fluoride component in said copolymer is from 50 to 98 wt%.
4. A method for the adhesion of vinylidene fluoride resins to metal substrates according to Claim 1, where the vinylidene fluoride resin is a mixture of from 1 to 99 wt% vinylidene fluoride homopolymer and from 99 to 1 wt% vinylidene fluoride copolymer resin according to Claim 3.
5. A method for the adhesion of vinylidene fluoride resins to metal substrates according to Claim 4, where the flexural modulus at room temperature of the vinylidene fluoride copolymer resin is no more than 1000 MPa.
6. A method for the adhesion of vinylidene fluoride resins to metal substrates according to any one of Claims 1 to 5 where the (b) component

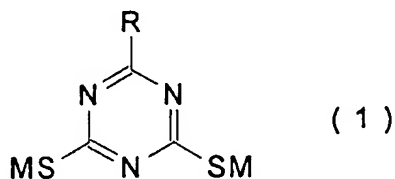


has at least one functional group selected from the carboxylic acid group and carboxylic acid anhydride group.

7. A method for the adhesion of vinylidene fluoride resins to metal substrates according to any one of Claims 1 to 6 where the organic compound used as the (c) component is an organic compound with a plurality of mercapto groups per molecule.

8. A method for the adhesion of vinylidene fluoride resins to metal substrates according to any one of Claims 1 to 6 where the organic compound used as the (c) component is an organic compound having at least one thioether group and at least one functional group selected from the carboxylic acid group, carboxylic acid anhydride group, ester group and amide group.

9. A method for the adhesion of vinylidene fluoride resins to metal substrates according to any one of Claims 1 to 6 which is characterized in that, as the organic compound used as the (c) component, there is added and mixed a 2-substituted-4,6-dimercapto-1,3,5-triazine derivative represented by the following formula



[where R denotes OR<sub>1</sub>, SR<sub>1</sub> or NR<sub>1</sub>R<sub>2</sub> (where R<sub>1</sub> and R<sub>2</sub> are the same or different and represent hydrogen, an alkyl group, cycloalkyl group, alkenyl group, aryl group, arylalkyl group or alkylaryl group), and M denotes hydrogen, an alkali metal or alkaline earth metal].

10. A method for the adhesion of vinylidene fluoride resins to metal substrates according to any one of Claims 1 to 6 where the organic compound used as the (c) component is a thioether carboxylic acid represented by the following formula, or anhydride thereof,



(where R<sub>3</sub> and R<sub>4</sub> are hydrocarbon groups with from 2 to 20 carbons, and m and n are the same or different integers in the range 1 to 4).

11. A method of producing an electrode structure which is  
5 characterized in that, to at least one face of a current collector, there is applied a slurry produced by mixing together an electrode active material and a solution formed by dissolving in an organic solvent from 0.5 to 50 parts by weight of (b) at least one type of polymer selected from acrylic and methacrylic polymers with functional groups which exhibit bonding  
10 properties or affinity in terms of metals, or an acrylic or methacrylic resin composition containing such polymer, and from 0.01 to 5 parts by weight of (c) an organic compound with at least one functional group selected from the mercapto group, thioether group, carboxylic acid group and carboxylic acid anhydride group, per 100 parts by weight of (a) vinylidene  
15 fluoride resin, and then the organic solvent is evaporated off.

12. A method of producing an electrode structure according to Claim 11 where the vinylidene fluoride resin is vinylidene fluoride homopolymer.

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13. A method of producing an electrode structure according to Claim 11 where the vinylidene fluoride resin is a copolymer of vinylidene fluoride and at least one monomer selected from tetrafluoroethylene, hexafluoropropylene, trifluoroethylene and trifluoro-chloroethylene, and the  
25 percentage vinylidene fluoride component in said copolymer is from 50 to 98 wt%.

14. A method of producing an electrode structure according to Claim 11 where the vinylidene fluoride resin is a mixture of from 1 to  
30 99 wt% vinylidene fluoride homopolymer and from 99 to 1 wt% vinylidene fluoride copolymer resin according to Claim 13.

15. A method of producing an electrode structure according to Claim 14 where the flexural modulus at room temperature of the  
35 vinylidene fluoride copolymer resin is no more than 1000 MPa.

16. A method of producing an electrode structure according to any one of Claims 11 to 15 where the (b) component has at least one functional group selected from the carboxylic acid group and carboxylic acid anhydride group.

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17. A method of producing an electrode structure according to any one of Claims 11 to 16 where the organic compound employed as the (c) component is an organic compound with a plurality of mercapto groups per molecule.

10

18. A method of producing an electrode structure according to any one of Claims 11 to 16 where the organic compound used as the (c) component is an organic compound having at least one thioether group and at least one functional group selected from the carboxylic acid group, carboxylic acid anhydride group, ester group and amide group.

15

19. A method of producing an electrode structure according to any one of Claims 11 to 16 where the organic compound used as the (c) component is a 2-substituted-4,6-dimercapto-1,3,5-triazine derivative as represented by Structural Formula 1 in Claim 9.

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20. A method of producing an electrode structure according to any one of Claims 11 to 16 where the organic compound used as the (c) component is a thioether carboxylic acid as represented by Structural Formula 2 in Claim 10, or anhydride thereof.

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21. A method of producing an electrode structure according to any one of Claims 11 to 20 where the total of the (a) component and (b) component used per 100 parts by weight of the electrode active material is from 1 to 50 parts by weight.

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22. An electrode structure produced by the method of any one of Claims 11 to 21.

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23. A non-aqueous battery which comprises a positive electrode, negative electrode and a separator layer disposed between the two electrodes, and at least one of said positive and negative electrodes comprises the electrode structure of Claim 22.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01272

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09J127/16 C09D127/16 C08L27/16 H01M4/62

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J C09D C08L H01M B05D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>WO 97 49777 A (ATOCHEM ELF SA ;BUSSI PHILIPPE (FR); MAILLET JEROME (JP); MIYAKI Y) 31 December 1997</p> <p>see page 1, line 33 - page 2, line 5 see page 2, line 31 - page 3, line 8 see page 3, line 26 - page 4, line 2 see page 5, line 25 - line 36 see page 6, line 19 - line 23 see claims 1,3</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	<p>1-4,6,7, 9,11-14, 16,17, 19,22,23</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/01272

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>PATENT ABSTRACTS OF JAPAN vol. 097, no. 007, 31 July 1997 &amp; JP 09 082314 A (ELF ATOCHEM JAPAN KK), 28 March 1997 cited in the application see abstract -&amp; DATABASE WPI Section Ch, Week 9723 Derwent Publications Ltd., London, GB; Class E19, AN 97-250897 XP002106365 &amp; JP 09 082314 A (ELF ATOCHEM JAPAN KK) , 28 March 1997 see abstract -&amp; CHEMICAL ABSTRACTS, vol. 127, no. 2, 14 July 1997 Columbus, Ohio, US; abstract no. 21009, MIYAKI, YOSHIYUKI ET ALL: "Lithium secondary batterie electrode and their manufacture" XP002106363 see abstract</p> <p>---</p>	<p>1-4,6,7, 9,11-14, 16,17, 19,22,23</p>
A	<p>WO 97 32347 A (ATOACHEM ELF SA ;GOTO KUNIYUKI (JP); MIYAKI YOSHIYUKI (JP); OHASHI) 4 September 1997 see page 2, line 9 - line 14 see page 2, line 26 - line 29 see page 3, line 12 - line 23 see page 4, line 11 - line 22 see examples 1,2</p> <p>---</p> <p style="text-align: center;">-/--</p>	<p>1-4,6, 11-14, 16,21-23</p>

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01272

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 097, no. 007, 31 July 1997 &amp; JP 09 082311 A (ELF ATOCHEM JAPAN KK), 28 March 1997 cited in the application see abstract -&amp; DATABASE WPI Section Ch, Week 9723 Derwent Publications Ltd., London, GB; Class L03, AN 97-250894 XP002106366 &amp; JP 09 082311 A (ELF ATOCHEM JAPAN) , 28 March 1997 see abstract -&amp; CHEMICAL ABSTRACTS, vol. 127, no. 2, 14 July 1997 Columbus, Ohio, US; abstract no. 21007, MYAKI, YOSHIYUKI ET AL: "Lithium secondary battery electrodes and their manufacture" XP002106364 see abstract</p> <p>---</p>	<p>1,7,11, 17,22</p>
A	<p>WO 97 27003 A (ATOACHEM ELF SA ;MIYAKI YOSHIYUKI (JP); OHASHI KAZUYOSHI (JP); KURA) 31 July 1997 see page 2, line 4 - page 3, line 6 see page 4, line 30 - line 37 see page 5, line 27 - line 30 see page 6, line 5 - line 7 see page 6, line 30 - line 36 see example 9</p> <p>---</p>	<p>1-4,6, 11-13, 16,21-23</p>
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